# [Supporting Information]

## Comprehensive Study of Medium-Bandgap Conjugated Polymer Merging a Fluorinated Quinoxaline with Branched Side Chains for High-Efficient and Air-Stable Polymer Solar Cells

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### Synthesis and Characterization

All other chemicals were purchased from commercial sources (Acros, Aldrich, TCI, and Solarmer Materials Inc.) and were used without further purification unless otherwise stated. All reactions were performed under nitrogen atmosphere and solvents were distilled from appropriate drying agents prior to use. The monomer 1,4-dibromo-2,3-difluoro-5,6-dinitrobenzene,[1] 1-bromo-3-((2-ethylhexyl)oxy) benzene (C1),[2] and 1,2-bis(3-((2-ethylhexyl)oxy)phenyl)ethane-1,2-dione (C2)[2] were synthesized according to modified procedure of reported literatures.[1,2] The synthetic route of F-QEH-2Br monomer is shown in Fig. S1 and the detailed synthetic processes are illustrated as follows.

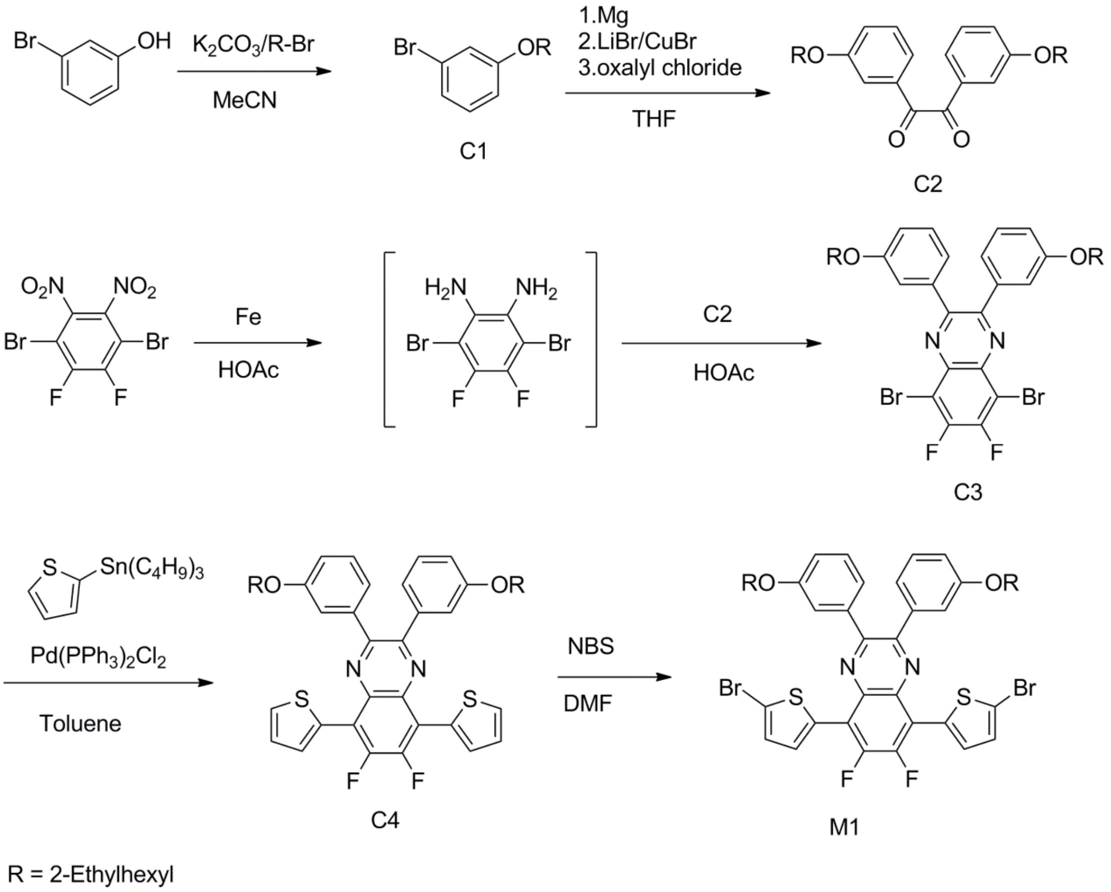

**Fig. S1.** Synthetic route of monomer M1.

**1-bromo-3-((2-ethylhexyl)oxy)benzene (C1)**

2-ethylhexyl bromide (34.26 mL, 179 mol), 3-bromopheno (25 g, 145 mmol), potassium carbonate (43.94 g, 318 mmol) were added into a round bottle with 150 mL acetonenitrile ($CH_3CN$) and reflux 12 h, then filtered. Afterwards, solvent was removed by rotary evaporation, then purified by column chromatography on silica gel (hexane) to afford compound C1 (20 g, 48.4%).

$^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.10 (t, $J$ = 8.4 Hz, 1H), 7.05~7.02 (m, 2H), 6.82~6.80 (m, 1H), 3.81~3.79 (d, $J$ = 5.6 Hz, 2H), 1.70 (m, $J$ = 1.2 Hz, 1H), 1.52~1.34 (m, 4H), 1.34~1.27 (m, 4H), 0.89~0.93 (m, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 160.22, 130.42, 123.45, 122.75, 117.76, 113.55, 70.72, 39.32, 30.48, 29.05, 23.84, 23.01, 14.04, 11.08. HRMS calcd for $C_{14}H_{21}BrO$: 284.0863, found: 284.0654

**1,2-bis(3-((2-ethylhexyl)oxy)phenyl)ethane-1,2-dione (C2)**

Solution of LiBr (12.17 g, 140 mmol) in tetrahydrofuran (THF, 40mL) was added to a stirred suspension of CuBr (10.06 g, 70 mmol) in tetrahydrofuran (THF, 50mL) at 0 ºC under nitrogen atmosphere. After stirred 20 min, the resulting mixture was added into well prepared Grignard reagent made of compound C1 (20.0 g, 70 mmol) and stirred at 0 ºC for 15 min, then into the mixture oxalyl chloride (2.6 mL, 30 mmol) was added and stirred at 0 ºC for 20 min. Afterward, the reaction mixture was poured into saturated aqueous $NH_4Cl$, extracted with ethyl acetate and dried with anhydrous $MgSO_4$. Solvent was removed by rotary vaporization purified with column chromatography on silica gel (hexane/DCM = 2/1) to afford compound C2 (10.9 g, 75%).

$^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.50 (t, 2H), 7.43 (m, 2H), 7.36 (t, $J$ = 15.6 Hz, 2H), 7.19~7.16 (m, 2H), 3.89~3.87 (d, $J$ = 5.8 Hz, 4H), 1.71 (m, 2H), 1.52~1.34 (m, 8H), 1.36~1.24 (m, 8H), 0.88 (m, 12H). $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 194.54, 159.88, 134.23, 129.92, 122.93, 122.22, 113.60, 70.83, 39.83, 30.48, 29.05, 25.63, 23.83, 23.00, 14.04, 11.08. HRMS calcd for $C_{30}H_{42}O_4$: 466.3113, found: 466.3083

**5,8-dibromo-2,3-bis(3-((2-ethylhexyl)oxy)phenyl)-6,7-difluoroquinoxaline (C3)**

1,4-dibromo-2,3-difluoro-5,6-dinitrobenzene (8.453 g, 23 mmol) and iron powder (11.76 g, 210 mmol) and acetic acid (HOAc, 100mL) were stirred at 50 ºC for 5 h. After filtering, compound C2 was added into the filtrate and heat under reflux for 12 h. The reaction mixture was poured into water and then extracted with DCM. Solvent was removed via rotary evaporation, and dried with anhydrous $MgSO_4$ then purified by column chromatography on silica gel (hexane/DCM = 3.5/1) to afford compound C3 (11.03 g, 65%).

$^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.27~7.23 (m, 2H), 7.20~7.15 (m, 4H), 6.95~6.92 (m, 2H), 3.70~3.68 (d, $J$ = 6.0 Hz, 4H), 1.66 (m, 2H), 1.49~1.25 (m, 16H), 0.89 (m, 12H). $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$): 159.30, 154.06, 138.75, 136.06, 129.37, 122.35, 16.72, 115.75, 109.66, 70.64, 39.18, 30.47, 29.02, 23.80, 23.04, 14.07, 11.32. $^{19}$F NMR ($CDCl_3$, 400 MHz, $\delta$): -119.59. HRMS calcd for $C_{36}H_{42}N_2O_2F_2Br_2$: 730.1647, found: 730.1581

**2,3-bis(3-((2-ethylhexyl)oxy)phenyl)-6,7-difluoro-5,8-di(thiophen-2-yl)quinoxaline (C4)**

Compound C3 (11.03 g, 15 mmol), 2-tri-*n*-butylstannyl thiophene (11.22 g, 30 mmol), and $Pd(PPh_3)Cl_2$ (0.53 g, 0.75 mmol) were heated under reflux in toluene for 48 h under nitrogen atmosphere. The solvent was removed via reduced pressure and purified by chromatography on silica gel (hexane/DCM = 3/1) to afford compound M4 (4.22 g, 37.9%).

$^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 8.04 (d, $J$ = 4.4Hz, 2H), 7.60 (d, $J$ = 5.6, 1.2 Hz, 2H), 7.35 (s, 2H), 7.26~7.22 (m, 6H), 6.95~6.92 (m, 2H), 3.77~3.75 (d, $J$ = 6 Hz, 4H), 1.70~1.66 (m, 2H), 1.45~1.24 (m, 16H), 0.91 (m, $J$ = 6.8 Hz, 12H). $^{13}$C NMR ($CDCl_3$, 100 MHz, $\delta$):159.31, 151.38, 139.22, 130.88, 130.79, 129.85, 129.14, 122.76, 116.70, 115.70, 70.69, 39.21, 30.53, 29.02, 23.87, 23.07, 14.09, 11.06. $^{19}$F NMR ($CDCl_3$, 400 MHz, $\delta$): -129.56. HRMS calcd for $C_{44}H_{48}N_2O_2F_2S_2$: 738.3186, found: 738.3125

**5,8-bis(5-bromothiophen-2-yl)-2,3-bis(3-((2-ethylhexyl)oxy)phenyl)-6,7-difluoro quinoxaline (M1)**

To a solution of C4 (3.16 g, 4.27 mmol) in dimethylforamide (DMF, 150 mL), solution of NBS (1.52 g, 8.54 mmol) in dimethylforamide (DMF, 30 mL) was added drop wise and heated to 40 ºC under nitrogen atmosphere for 3 h. Afterward, to the mixture water was added and extracted with DCM. Solvent was removed via rotary evaporation, and dried with anhydrous $MgSO_4$ then purified by column chromatography on silica gel (hexane/DCM = 6/1) to afford compound M1 (2.88 g, 75.1%).

$^1$H NMR ($CDCl_3$, 400 MHz, $\delta$): 7.79 (d, $J$ = 4.0 Hz, 2H), 7.43 (m, 2H), 7.20 (d, $J$ = 8 Hz, 2H), 7.16 (d, $J$ = 5.6, 1.6 Hz, 2H),7.09~7.07 (m, 2H), 6.97 ~6.95 (m, 2H), 3.89~3.82 (m, $J$ = 13.2 Hz, 4H), 1.72~1.68 (m, 2H), 1.50~1.39 (m, 8H), 1.32~1.30 (m, 8H), 0.94~0.87 (m, 12H). $^{13}$C

NMR ($CDCl_3$, 100 MHz, $\delta$):159.59, 151.85, 138.74, 132.46, 132.41, 130.95, 129.39, 129.12, 122.79, 118.90, 117.07, 115.36, 70.65, 39.42, 30.59, 29.16, 23.93, 23.08, 14.10, 11.23. $^{19}F$ NMR ($CDCl_3$, 400 MHz, $\delta$): -129.34. HRMS calcd for $C_{44}H_{46}N_2O_2F_2Br_2S_2$: 896.7856, found: 896.7715

**poly{4,8-bis(2'-ethylhexyloxy)-benzo[1,2-b:4,5-b']dithiophene-alt-[5,8-bis(5'-thiophen-2'-yl)-6,7-difluoro-2,3-bis(3''-(2-ethylhexyl)oxyphenyl)quinoxaline]} (PBDTQEH)**

Compound M1 (0.336 g, 0.375 mmol), (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b'] dithiophene-2,6-diyl)bis(trimethylstannane) (0.290 g , 0.375 mmol) and $Pd(PPh_3)_4$ (0.022 g, 5 mol% relative to M1) were heated in 100 mL xylene in microwave reactor: 140 ° C for 30 min and 170 ° C for 120 min. Afterward, the solution was allowed to cooling down, and crude polymer was precipitated into methanol and filtered, followed by careful washing with methanol (overnight), acetone (overnight), dichloromethane (6 h) and chloroform (4 h) to remove byproducts and oligomers. The final product was obtained via extraction from the chloroform fraction precipitated into methanol, filtered and dried under vacuum for 12 h.

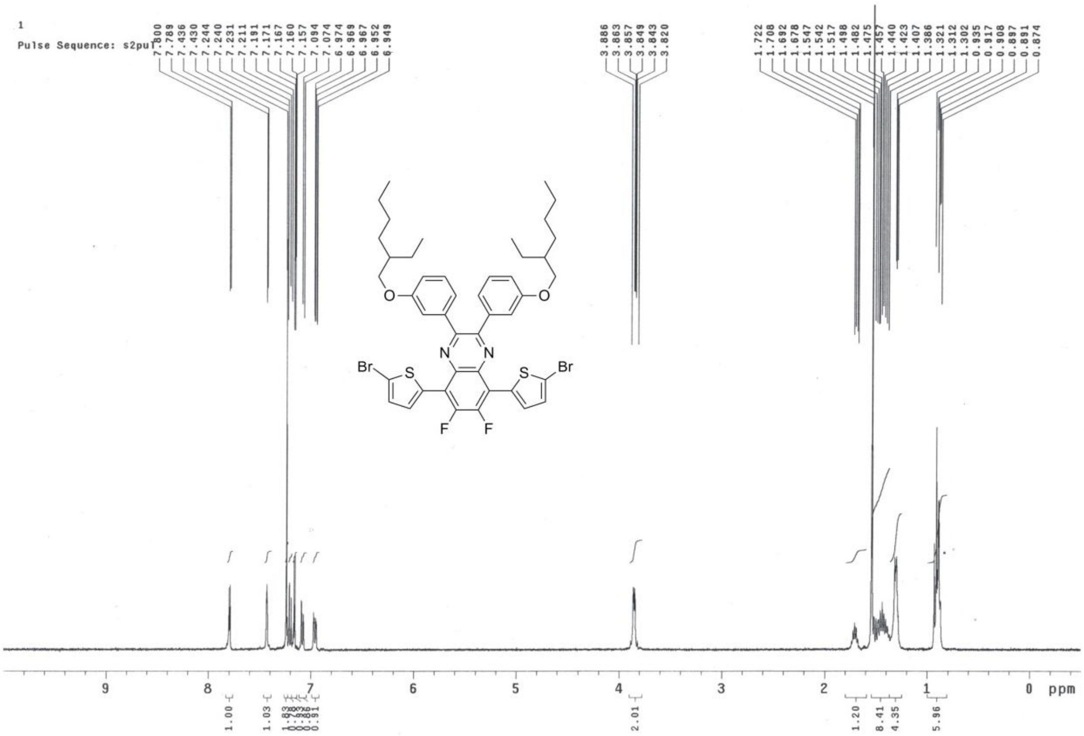

Fig. S2. $^1$H-NMR spectrum of compound M1.

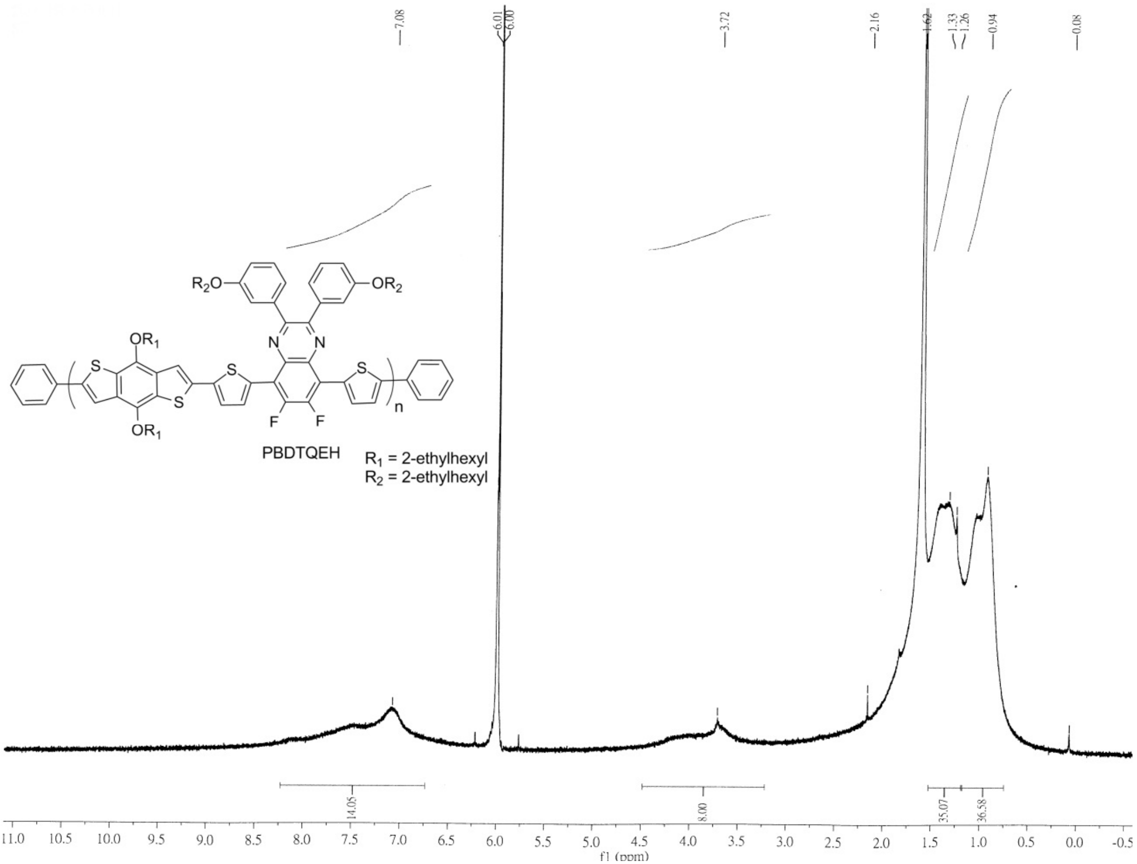

Fig. S3. $^1$H-NMR spectrum of polymer PBDTQEH.

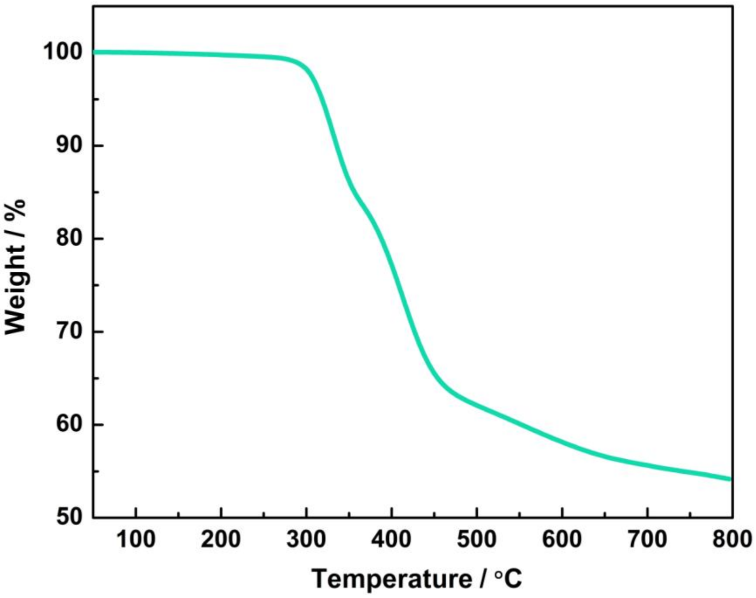

**Fig. S4.** Thermogravimetric analysis (ramp rate: 10 °C min$^{-1}$) of PBDTQEH copolymer. The purge gas for TGA was nitrogen.

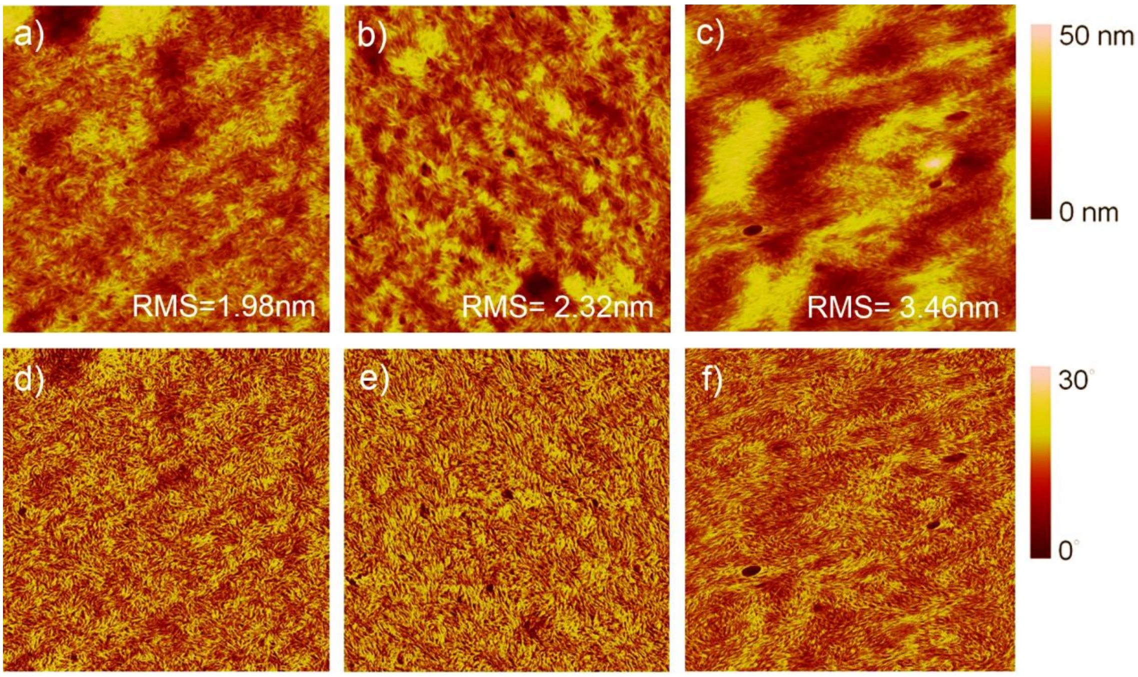

**Fig. S5.** TM-AFM (a–c) topography and (d–f) phase images of PBDTQEH:PC$_{71}$BM blend films with various compositions: (a,d) 1:0.5; (b,e) 1:1; and (c,f) 1:2. The imaging size is 2 μm × 2 μm.

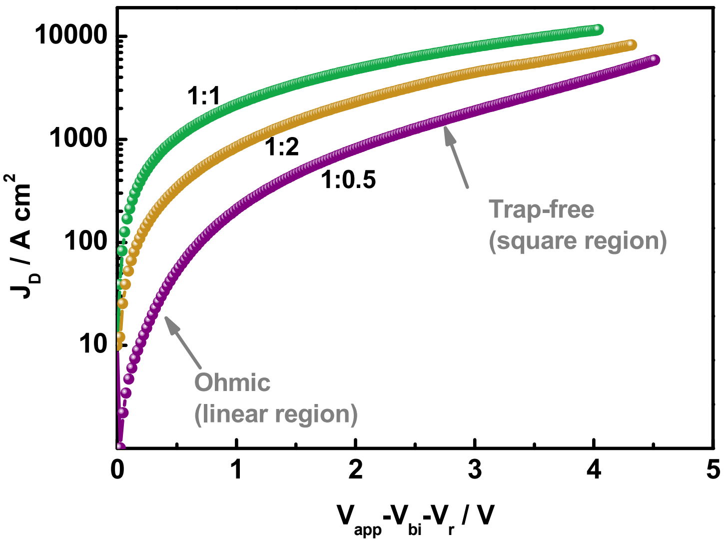

**Fig. S6.** Determination of the hole mobility from the dark current densities for PBDTQEH:PC$_{71}$BM diodes with various compositions (symbols). The solid lines are fits of the data points. The applied voltage was corrected for the built-in voltage ($V_{bi}$) arising from the work function difference between the contacts and the voltage loss ($V_r$) due to contact resistance and series resistance across the electrodes. The thickness of the films is indicated in the plots.

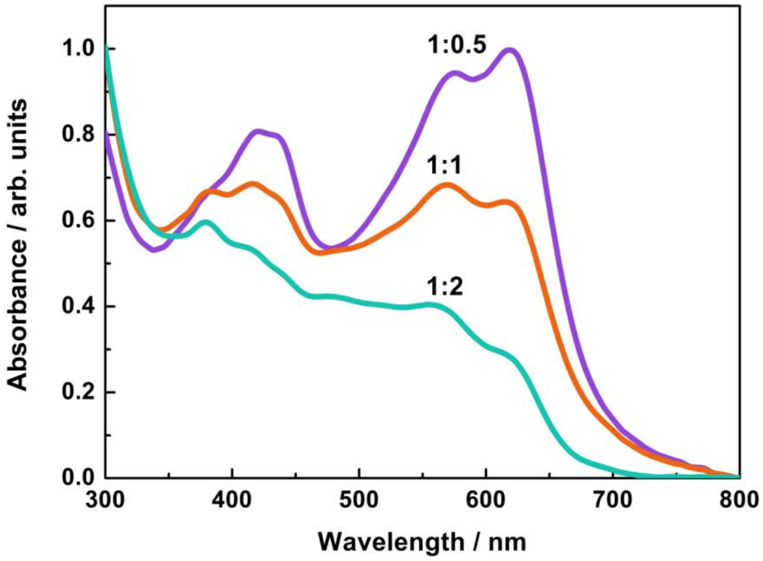

**Fig. S7.** UV-vis spectra of PBDTQEH:PC$_{71}$BM blend films. The presence of vibronic features at ~ 618 nm in the absorption spectra of the polymer blends further corroborates ordering of the polymer.

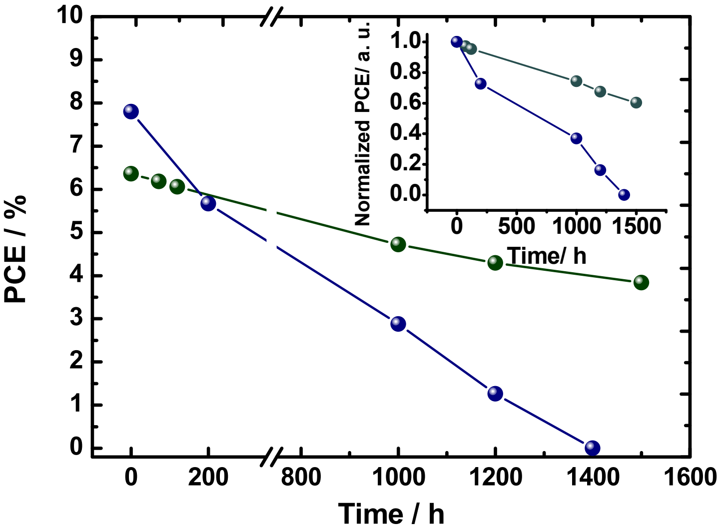

**Fig. S8.** Air stability tests of PBDTQEH:$PC_{71}BM$ (green line) and PBDT-TFQ:$PC_{71}BM$ (blue line) solar cells upon inverted configurations in ambient atmosphere as a function of storage time.

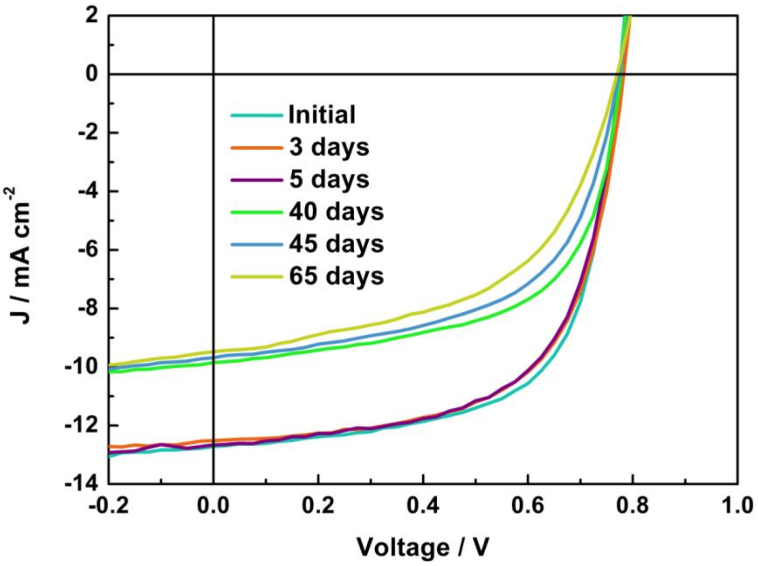

**Fig. S9**. *J–V* characteristic of the inverted cell as a function of storage time in ambient air.

**Table S1.** Representative photovoltaic performance for 1:1 PBDTQEH:PC$_{71}$BM device without encapsulation as a function of storage time in ambient air.

| Times [h] | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF [%] | PCE [%] |
|---|---|---|---|---|
| initial | 0.78 | 12.72 | 64.3 | 6.36 |
| 72 | 0.78 | 12.51 | 62.9 | 6.15 |
| 120 | 0.78 | 12.66 | 61.8 | 6.08 |
| 1000 | 0.78 | 9.86 | 60.7 | 4.69 |
| 1200 | 0.76 | 9.69 | 57.2 | 4.21 |
| 1500 | 0.76 | 9.51 | 52.5 | 3.79 |

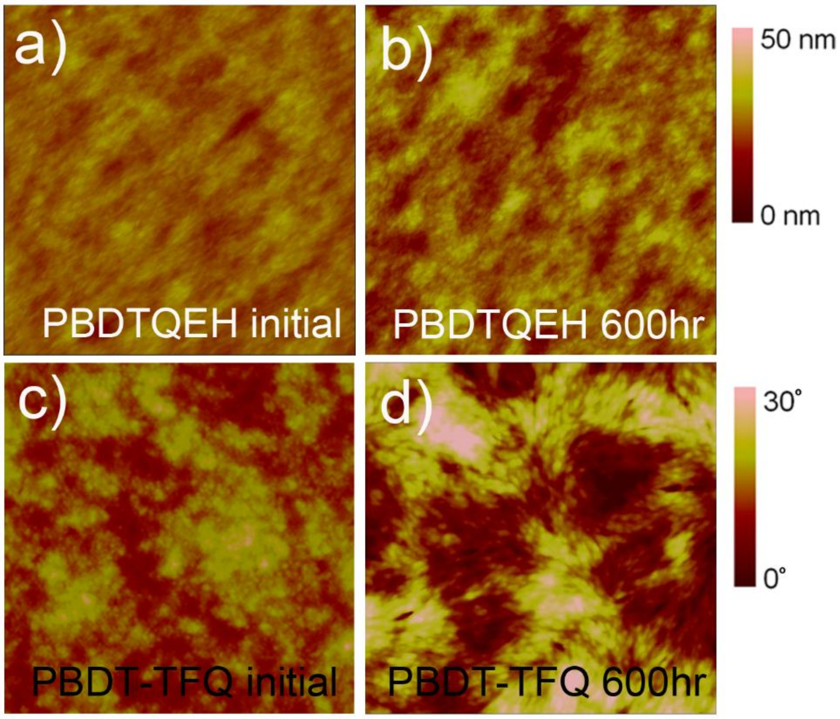

**Fig. S10**. Evolution of morphologies tests of PBDTQEH:$PC_{71}BM$ and PBDT-TFQ:$PC_{71}BM$ solar cells upon inverted configurations in ambient atmosphere.

## Reference

1 Z. Li, J. P. Lu, S.-C. Tse, J. Y. Zhou, X. M. Du, Y. Tao and J. F. Ding, *J. Mater. Chem.*, 2011, **21,** 3226-3233.

2 A. Gadisa1, W. Mammo, L. M. Andersson, S. Admassie, F. Zhang, M. R. Andersson and O. Inganäs, *Adv. Funct. Mater.*, 2007, **17,** 3836-3842.